CALIFORNIA
ENERGY
COMMISSION

ENERGY INNOVATIONS SMALL GRANT PROGRAM
Environmentally Preferred Advanced Generation

Novel Composite Membranes for Fuel Cells

FEASIBILITY ANALYSIS

March 2003
P500-03-017F

Gray Davis, *Governor*

CALIFORNIA ENERGY COMMISSION

Prepared By:
Hal Clark
Grant Program Administrator
San Diego State University Foundation

Prepared For:
California Energy Commission
Energy Innovations Small Grant Program

Researcher:
Sossina M. Haile
California Institute of Technology

Grant Number:
99-19

LEGAL NOTICE

PREFACE

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable and reliable energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Commission), annually awards up to $62 million of which $2 million/year is allocated to the Energy Innovation Small Grant (EISG) Program for grants. The EISG Program is administered by the San Diego State University Foundation under contract to the California State University, which is under contract to the Commission.

The EISG Program conducts four solicitations a year and awards grants up to $75,000 for promising proof-of-concept energy research.

PIER funding efforts are focused on the following six RD&D program areas:

- Residential and Commercial Building End-Use Energy Efficiency
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy Technologies
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Strategic Energy Research

The EISG Program Administrator is required by contract to generate and deliver to the Commission a Feasibility Analysis Report (FAR) on all completed grant projects. The purpose of the FAR is to provide a concise summary and independent assessment of the grant project using the Stages and Gates methodology in order to provide the Commission and the general public with information that would assist in making follow-on funding decisions (as presented in the Independent Assessment section).

The FAR is organized into the following sections:

- Executive Summary
- Stages and Gates Methodology
- Independent Assessment
- Appendices
    - Appendix A: Final Report (under separate cover)
    - Appendix B: Awardee Rebuttal to Independent Assessment (Awardee option)

For more information on the EISG Program or to download a copy of the FAR, please visit the EISG program page on the Commission's Web site at:
http://www.energy.ca.gov/research/innovations

or contact the EISG Program Administrator at (619) 594-1049 or email eisgp@energy.state.ca.us.

For more information on the overall PIER Program, please visit the Commission's Web site at http://www.energy.ca.gov/research/index.html.

Executive Summary

Introduction

Fuel cells utilizing a polymer electrolyte membrane (PEM) have the desirable characteristics that they operate at near room temperature with high power density. A less desirable characteristic of the proton-conducting polymer is that it utilizes water, in the form of the hydronium ions, H_3O^+, as the proton conductor. This leads to a requirement for water re-circulation and temperature control in the system. In addition, the need to maintain hydration limits the maximum allowable temperature and results in low efficiency in hydrogen-air fuel cells. PEM fuel cell operating at higher temperatures can demonstrate improved efficiency and reduced carbon monoxide poisoning of the catalyst.

If a substitute for the hydrous component in the fuel cell membrane were found, manufacturers could eliminate the need for water re-circulation, relieve thermal management issues and achieve the benefits of higher temperature operation's increase of catalyst efficiency in generating protons at the fuel cell anodes. This benefit is directly applicable to all PEM fuel cells including hydrogen/air fuel cells, and cells fueled by reformed hydrocarbons. These fuel cells are typical of those applied to power generation.

Many solid acids exhibit excellent proton transport properties, but less than ideal mechanical properties and chemical stability. For these reasons, the researcher selected and investigated composite materials utilizing an inert polymer matrix to support the embedded solid acid.

Objectives

The goal of this project was to determine the feasibility of using proton-conducting membranes that do not rely on hydrated polymer for proton transport in a PEM fuel cell. The proposed membranes are composites of inert polymers and "solid acids." The following project objectives were established:

1. Prepare, characterize and evaluate a broad range of polymer/solid acid composite membranes for subsequent development of membrane electrode assemblies.
2. Fabricate and Characterize electrodes and membrane-electrode assemblies. Understand and optimize electrode microstructure.
3. Demonstrate a single cell fuel cell utilizing a sold acid based membrane operating at temperatures between 100 and 180^{o}C.

Outcomes

1. A large number of composite membrane systems (more than 12) were prepared, characterized and evaluated. The majority of these systems exhibited low conductivities and poor homogeneity, although some, notably composites formed using a ceramic matrix, had conductivities within an order of magnitude of the solid acid alone and excellent reproducibility. Because of the higher conductivity of the solid acid alone, such membranes (in which the inert matrix material was eliminated) were used for further fuel cell development.
2. Membrane electrode assemblies were fabricated using various techniques. The most successful technique discovered was the simultaneous cold-pressing of the electrode/electrolyte/catalyst layers and the electrolyte membrane material. A volatile organic

(naphthalene) was added to assure porosity. These assemblies were very thick because of the need to assure impermeability of the solid acid layer.

3. Fuel cells were demonstrated using several variations of electrode/electrolyte/catalyst layers. They can be generally characterized as exhibiting an open circuit voltage ranging from 1 to 1.12 volts, and producing power ranging up to 12 mW/cm^2.
4. An unanticipated outcome of this research was the discovery that in a reducing environment (flowing hydrogen) the sulfur content in the solid acid reduced to H_2S. The rate of conversion was higher in the presence of a metal catalyst. This chemical reaction limits the long-term stability of these fuel cells. Solid acids not containing sulfur were shown to be stable, but as of yet no solid acid combining high stability and high conductivity has been identified.

Conclusions

Knowledge was gained and conclusions were drawn from each step in the progress of this project as detailed in Appendix A. The researcher summarized the project in these words; "The problem of sulfur (or selenium) reduction has proved vexing indeed. The development of optimized membrane electrode assembly structures awaits the discovery of alternative solid acids with greater chemical stability (materials that exclude sulfur and selenium)." This project determined that the use of proton conducting membranes that do not rely on hydrated polymers for proton transport in PEM fuel cells is not feasible using *current* solid acid materials.

Benefits to California

In this project it was demonstrated that the path to a successful energy product that will benefit California electric ratepayers requires as its first step the development of alternative solid acid materials. It cannot be predicted at the outset whether such materials will be discovered.

Recommendations

The basic thesis for this project was sound and the research was carried out in a professional and competent manner. Unfortunately the chemistry involved did not result in a usable anhydrous membrane material. If one is to realize the potential advantages of anhydrous, thermally stable proton conductors, “alternate solid acids with greater chemical stability" must first be discovered.

Appendix A: Final Report (under separate cover)

Appendix B: Awardee Rebuttal to Independent Assessment (none submitted)